

(54) FLOCKED LAMINATED SHEET

- (11) 5-254046 (A) (43) 5.10.1993 (19) JP
 (21) Appl. No. 4-53758 (22) 12.3.1992
 (71) SHOWA HIGHPOLYMER CO LTD(2) (72) SEIICHI KOBAYASHI(4)
 (51) Int. Cl⁵. B32B5/16, B32B5/02, B32B7/10, B32B27/20, B32B27/32

PURPOSE: To obtain a uniformly flocked product enhanced in adhesiveness and rigidity and good in moldability by laminating a flocked film obtained by flocking the surface of a non-stretched propylene type film with staple fibers to the surface of a main layer composed of a propylene resin containing a specific inorg. filler.

CONSTITUTION: A main layer is composed of a resin compsn. consisting of 30-90wt.% of a propylene type resin with a melt flow rate of 0.01-5g/10min and 10-70wt.% of an inorg. filler such as metal, aluminum oxide, calcium hydroxide or magnesium oxide. A flocked film obtained by flocking a non-stretched propylene type resin film subjected to chemical and mechanical surface treatment in order to enhance the adhesiveness with an adhesive with staple fibers composed of natural or synthetic fibers through an adhesive is laminated to the surface of the main layer.

(54) MOLDED INTERIOR PRODUCT FOR VEHICLE

- (11) 5-254047 (A) (43) 5.10.1993 (19) JP
 (21) Appl. No. 4-55038 (22) 13.3.1992
 (71) SEKISUI CHEM CO LTD (72) HIROBUMI INOUE(2)
 (51) Int. Cl⁵. B32B5/18, B29C43/18, B32B7/02, B32B27/32//B29K23/00, B29K105/04, B29L31/58

PURPOSE: To provide a molded interior product almost uniform in elongation in its thickness direction and prevented from trouble such as the destruction of foam at the time of molding due to a stamping molding method by using polypropylene foam whose elongations at three stages of temps. are adjusted so as to enter the specific range of the average value of the elongation values.

CONSTITUTION: A skin material is laminated to one surface of polyolefinic foam and a thermoplastic resin for aggregate is integrally molded on the other surface thereof by a stamping molding method. Herein, the polyolefinic foam is adjusted so that the elongations (a), (b), (c) thereof at 50, 120, 160°C are enter the range of $\pm 30\%$ of the average value of the elongation values. Further, polypropylene type foam composed of a propylene homopolymer or a propylene/other olefin or vinyl acetate copolymer having apparent densit 0.10g/cm³ or less and a gel ratio of 40% or more is used.

(54) LAMINATED SHEET

- (11) 5-254048 (A) (43) 5.10.1993 (19) JP
 (21) Appl. No. 4-53650 (22) 12.3.1992
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 (51) Int. Cl⁵. B32B5/28, B32B7/02, B32B17/04, B32B27/04, B32B27/34, H05K1/03

PURPOSE: To enhance reinforcing effect in a thickness direction and to improve a flaw due to difference in the coefficient of thermal expansion at the time of the loading of a printed wiring board with a chip part by using a fabric composed of spun yarn wherein cut glass fibers and org. fibers having the negative coefficient of thermal expansion are mixed in a monofilament state in a resin impregnated base material.

CONSTITUTION: A laminate is formed by laminating a predetermined number of resin impregnated base materials. As the resin of the resin impregnated materials, a phenol resin, a cresole resin or an epoxy resin is used. As at least one base material among the resin impregnated base materials, a fabric composed of a fiber mixture obtained by opening the aggregate of cut glass fibers and org. fibers having the negative coefficient of thermal expansion composed of full-aromatic polyamide fibers, especially, para-aramide fibers and mixing the opened fibers by a mix spinning machine and carding the mixed fibers by a spinning card machine is used.

(19)日本国特許庁(J P)

(12) 公 開 特 許 公 報 (A)

(11)特許出願公開番号

特開平5-254048

(43)公開日 平成5年(1993)10月5日

(51)Int.Cl. ⁵	識別記号	庁内整理番号	F I	技術表示箇所
B 3 2 B	5/28	A	7016-4F	
	7/02	1 0 5	7188-4F	
	17/04			
	27/04	Z	7717-4F	
	27/34		7016-4F	

審査請求 未請求 請求項の数2(全 3 頁) 最終頁に続く

(21)出願番号 特願平4-53650

(22)出願日 平成4年(1992)3月12日

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(54)【発明の名称】 積層板

(57)【要約】

【構成】カットされたガラス繊維糸と負の熱膨脹係数を有する有機繊維糸、例えばパラ系全芳香族ポリアミド繊維糸からなる紡績糸を用いて製織された織布を少なくとも1枚樹脂含浸基材として構成した積層板を得る。

【効果】積層板として低い熱膨脹係数を有し、かつ紡績糸を使用していることより厚み方向にも優れた補強効果を有し、その結果、印刷配線板のチップ部品搭載時の熱膨脹係数の違いによる欠陥改善に大いに役立つ。

【特許請求の範囲】

【請求項1】 樹脂含浸基材を所定枚数積層成形してなる積層板であって、樹脂含浸基材のうち少なくとも1枚の基材が、カットされたガラス繊維糸と、負の熱膨張係数を有する有機繊維糸とを単繊維の状態で混合した紡績糸を用いて製織された織布であることを特徴とする積層板。

【請求項2】 負の熱膨張係数を有する有機繊維糸がパラ系全芳香族ポリアミド繊維糸からなる紡績糸であることを特徴とする請求項1の積層板。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は積層板に関し、さらに詳しくは電子機器、電気通信機器、産業機器等に使用される印刷配線板用積層板に関する。

【0002】

【従来の技術】近年、電子機器の小型軽量化、高密度化の観点から、これに組み込んで使用される電子部品はリード付部品からチップ部品へ急速に移行しており、さらにその実装方法も表面実装が主流になってきている。これに伴い印刷配線板の材料である積層板に対してこれまで以上の厳しい性能が要求されている。特にチップ部品搭載時の使用される材料の熱膨張係数の違いによる接合部の欠陥が大きな問題となっている。これは通常使用されるICやトランジスタ等のチップ部品の熱膨張係数が $2 \sim 7 \times 10^{-6}/^{\circ}\text{C}$ であり、一方該チップを搭載する一般的な基板であるガラスエポキシ樹脂基板の熱膨張係数が $10 \sim 20 \times 10^{-6}/^{\circ}\text{C}$ と大きいことに起因している。

【0003】これに対して、従来、芳香族ポリアミド繊維糸を用いた積層板（特公平2-59637）、石英繊維糸を用いた積層板（特公平3-227）および石英繊維糸とガラス繊維糸とを用いて製織された複合布を用いた積層板（特公平3-226）によって問題を解決する試みがなされているが、パラ系全芳香族ポリアミド繊維を単独に用いた積層板の場合、パラ系全芳香族ポリアミド繊維の有する負の熱膨張係数および高強度のために樹脂中にクラックが生じる問題がある。また、石英繊維糸および石英繊維布はコストが高く、その用途が限定されている。

【0004】

【発明が解決しようとする課題】本発明の目的は、前記のような熱膨張係数が改善された、特に表面実装に適した印刷配線板用の積層板を提供することにある。

【0005】

【課題を解決するための手段】上記課題を解決するための本発明の構成は、樹脂含浸基材を所定枚数積層成形してなる積層板であって、樹脂含浸基材のうち少なくとも1枚の基材が、カットされたガラス繊維糸と、負の熱膨張係数を有する有機繊維糸、例えばパラ系全芳香族ポリ

アミド繊維糸とからなる紡績糸を用いて製織された織布であることを特徴とする積層板である。以下、本発明を詳細に説明する。

【0006】積層板に代表される複合材料の熱膨張係数は補強材の熱膨張係数によって支配され、本発明のように混合繊維紡績糸を補強材とする場合、その混合繊維の体積分率の和によって決定される。そのため、負の熱膨張係数を有する有機繊維糸、例えばパラ系全芳香族ポリアミド繊維糸と正の熱膨張係数を有するガラス繊維糸を設定した比率で組合わせると任意の熱膨張係数を有する積層板用基材を得ることができる。しかしながら、単に両繊維を混合した場合、繊維分布と同様な積層板中での熱膨張係数の分布が生じ、積層板のそり、ねじれ、ミクロクラック、寸法変化等の問題を引き起こす。さらに、ドリル加工性等に代表される積層板の加工性もまた易加工性のガラス繊維と、例えば難加工性のパラ系全芳香族ポリアミド繊維とが不均一に分布している場合、積層板全体としての加工性の低下を引き起こす。これらの問題を回避するためには両繊維を単繊維の状態で混合した複合紡績糸が必要である。このような紡績糸を使用した織布を積層板に用いると、糸束内に樹脂が含浸し易く、樹脂と補強材が均一に混在した状態になり、厚み方向に対する補強材の効果も従来の連続長繊維による織布を用いた場合よりも大きくなる。

【0007】本発明において、カットされたガラス繊維と、負の熱膨張係数を有する有機繊維糸を単繊維状態で混合した混合紡績糸を得る方法としては、例えば原料、つまりカットされたガラス繊維と負の熱膨張係数を有する有機繊維の集合体とを開繊し、混紡機により混合し、紡績カード機によりカーディングして得られた混合繊維スライバーを精紡することにより得られる。

【0008】また、該紡績糸を用いて製織する織布としては、あや織り、朱子織り、平織り等の織布が可能であるが、積層板の寸法安定性を向上させるために、平織り布を用いることが望ましい。本発明に用いられるカットされたガラス繊維は特に限定されるものではなく、電気特性の優れたEガラス、低誘電率のDガラス、シリカガラス等を使用することができる。また、その繊維径は通常用いられる $2 \sim 15$ ミクロンの範囲のものが使用されるが、目的に応じて数種類の径の繊維が混合して用いることができる。繊維長もまた通常紡績に使用される $25 \sim 75$ mmの繊維が使用できる。

【0009】さらに、負の熱膨張係数を有する有機繊維としては全芳香族ポリアミド繊維、特にパラ系アラミド繊維が好ましく、例えばデュボン社製のケブラー、帝人社製のテクノーラ（いずれも商標）等があげられる。これらの繊維の形状は紡績加工が可能であるならば特に限定されず、またチョップドファイバーでもステープルファイバーのいずれでもよい。本発明に用いられる樹脂含浸基材の樹脂としては、フェノール樹脂、クレゾール樹

脂、エポキシ樹脂、不飽和ポリエステル樹脂、ポリイミド樹脂、ポリブタジエン樹脂、ポリアミド樹脂、ポリフェニレンオキサイド樹脂、フッ素樹脂等の単独、変成物、混合物等を用いることが可能であり、用途に合わせて適宜選択される。本発明において、上記ガラス繊維糸と上記有機繊維糸の混合紡績糸の混合比率はまた選択された樹脂に合わせて適宜決定される。すなわち、好ましくはガラス繊維糸、有機繊維糸および樹脂のそれぞれの体積比で案分して計算された熱膨張係数の総和がゼロになるように決定される。本発明による積層板は通常のガラス繊維補強積層板の製造設備で常法に従って製造される。

【0010】

【実施例】以下、実施例を示して本発明を具体的に説明するが、本発明は実施例に限定されるものではない。

実施例

繊維径10ミクロンEガラス50mmチョップドストランドおよびテクノーラ（帝人社製のパラ系ポリアラミド繊維の商品名）51mmチョップドファイバーをオープナー*

で開繊し、体積比率で1:1になるように計量し混紡機で混合綿とした。該混合綿をローカード機によりカーディングし、混合スライバーを作成し、従来のリング紡績機で紡績加撚し、71Tex (g/1000m)の複合紡績糸を得た。次いで、該複合紡績糸を密度が径32本/25mm、緯30本/25mmからなり、織組織が平織りからなる織布に製織し、エポキシ樹脂ワニスを含浸させ、乾燥して得たプリプレグを使用して、樹脂含量45重量%の2mm厚の積層板を得た。表1に該積層板の熱膨張係数の測定結果を示す。

比較例

平織りガラス繊維織布（経糸および緯糸ECG75-1/0で密度が44×32本/インチ、重量が219g/m²のスタイル7628、旭シェーベル社製）に、エポキシ樹脂ワニスを含浸させ、乾燥して得たプリプレグを使用して、樹脂含量45重量%の2mm厚の積層板を得た。表1に該積層板の熱膨張係数の測定結果を示す。

【0011】

【表1】

	熱膨張係数 (mm/mm・℃)	
	XY方向 (平面方向)	Z方向 (厚み方向)
実施例	6.5×10 ⁻⁶	15×10 ⁻⁶
比較例	15×10 ⁻⁶	47×10 ⁻⁶

【0012】

【発明の効果】本発明の積層板は、特定の2種の繊維糸の混合紡績糸を用いているので、積層板としたときに低い熱膨張係数を有し、かつ紡績糸を使用していることよ※

※り厚み方向にも優れた補強効果を有する。その結果、本発明の積層板を使用した印刷配線板のチップ部品搭載時の熱膨張係数の違いによる欠陥改善に役立つ。

フロントページの続き

(51) Int. Cl. ⁵

H05K 1/03

識別記号

庁内整理番号

K 7011-4E

F I

技術表示箇所

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CLAIMS

[Claim(s)]

[Claim 1] The laminate characterized by being the laminate which comes to carry out predetermined number-of-sheets laminate molding of the resin sinking-in base material, and being the textile fabrics with which weaving of the base material of at least one sheet was carried out using the spun yarn which mixed the cut glass fiber thread and the organic fiber thread which has a negative coefficient of thermal expansion in the state of the single fiber among resin sinking-in base materials.

[Claim 2] The laminate of the claim 1 characterized by being spun yarn with which the organic fiber thread which has a negative coefficient of thermal expansion consists of Para system all aromatic-polyamide fiber thread.

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JP 5-254048

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the laminate for printed circuit boards used for electronic equipment, a telecommunication device, an industrial device, etc. in more detail about a laminate.

[0002]

[Description of the Prior Art] In recent years, the electronic parts used from a viewpoint of the formation of small lightweight of electronic equipment and densification, including in this have shifted to the chip quickly from parts with a lead, and, also in the mounting method, a surface mount is becoming in use further. In connection with this, the severe performance more than the former is demanded from the laminate which is the material of a printed circuit board. The defect of the joint by the difference in the coefficient of thermal expansion of the material for which it is used especially at the time of chip loading poses a big problem. It originates in this having the coefficient of thermal expansion of the glass epoxy resin substrate the coefficient of thermal expansion of chips, such as IC usually used and a transistor, is $2 - 7 \times 10^{-6} / \text{degree C}$, and is [substrate] the general substrate in which this chip is carried on the other hand as large as $10 - 20 \times 10^{-6} / \text{degree C}$.

[0003] On the other hand, the laminate using former and aromatic-polyamide fiber cloth (JP,2-59637,B), Although the attempt which solves a problem by the laminate (JP,3-226,B) using the compound cloth by which weaving was carried out using the laminate (JP,3-227,B) and quartz-fiber thread using the quartz-fiber cloth, and glass fiber thread is made, in the case of the laminate using Para system all aromatic-polyamide fiber, there is a problem which a crack produces in a resin independently for the strong force [quantity / the negative coefficient of thermal expansion which Para system all aromatic-polyamide fiber has, and]. Moreover, quartz-fiber thread and a quartz-fiber cloth have high cost, and the use is limited.

[0004]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the laminate for printed circuit boards suitable for especially the surface mount by which the above coefficients of thermal expansion have been improved.

[0005]

[Means for Solving the Problem] The composition of this invention for solving the above-mentioned technical problem is a laminate which comes to carry out predetermined number-of-sheets laminate molding of the resin sinking-in base material, and it is the laminate characterized by being the textile fabrics by which weaving was carried out using the spun yarn with which the base material of at least one sheet consists of cut glass fiber thread, and the organic fiber thread with which it has a negative coefficient of thermal expansion, for example, Para system all aromatic-polyamide fiber thread, among resin sinking-in base materials. Hereafter, this invention is explained in detail.

[0006] The coefficient of thermal expansion of the composite material represented by the laminate is determined by the sum of the volume fraction of the mixed fiber, when the coefficient of thermal expansion of reinforcing materials rules over and it makes mixed fiber spun yarn into reinforcing materials like this invention. Therefore, if it combines by the ratio which set up the organic fiber thread which has a negative coefficient of thermal expansion, for example, Para system all aromatic-polyamide fiber thread, and the glass fiber thread which has a positive coefficient of thermal expansion, the base material for laminates which has arbitrary coefficients of thermal expansion can be obtained. However, when both fiber is only mixed, a fiber distribution and the distribution of the coefficient of thermal expansion in the inside of the same laminate arise, and problems, such as a warp of a laminate, torsion, a micro crack, and a dimensional change, are caused. Furthermore, the processability of the laminate represented by drilling nature etc. also causes the fall of the processability as the whole laminate, when the glass fiber of ***** and the Para system all aromatic-polyamide fiber of for example, difficulty processability are distributed unevenly. In order to avoid these problems, the compound spun yarn which mixed both fiber in the state of the single fiber is required. If the textile fabrics which used such spun yarn are used for a laminate, a resin will tend to sink in into a thread, it will be uniformly intermingled by a resin and reinforcing materials, and the effect of reinforcing materials over the thickness direction will also become larger than the case where the textile fabrics by the conventional continuous glass fiber are used.

[0007] As a method of obtaining the mixed spun yarn which mixed the organic fiber thread which has a negative coefficient of thermal expansion with the cut glass fiber in the state of the single fiber in this invention, the aggregate of a raw material, i.e., the cut glass fiber, and the organic fiber which has a negative coefficient of thermal expansion is opened, for example, and it mixes with a mixed machine, and is obtained by carrying out fine spinning of the mixed fiber sliver obtained by carrying out carding by the spinning carding machine.

[0008] moreover -- as the textile fabrics which carry out weaving using this spun yarn -- a twilled weave and Chu-tzu -- although

textile fabrics, such as textile and a plain weave, are possible, in order to raise the dimensional stability of a laminate, it is desirable to use a plain-weave cloth. Especially the cut glass fiber that is used for this invention is not limited, and can use the E glass which was excellent in the electrical property, the D glass of a low dielectric constant, a silica glass, etc. Moreover, according to the purpose, the fiber of some kinds of paths can be mixed and the diameter of fiber can be used, although the thing of the range of 2-15 microns usually used is used. The 25-75mm fiber for which fiber length is also usually used for spinning can be used.

[0009] Furthermore, the Du Pont Kevlar, theque NORA (all are trademarks) by Teijin, Ltd., etc. are raised preferably [all aromatic-polyamide fiber, especially the Para system aramid fiber] as organic fiber which has a negative coefficient of thermal expansion. Especially if spinning processing is possible for the configuration of these fiber, it may not be limited, and chopped fiber or any of a staple fiber is sufficient as it. As a resin of a resin sinking-in base material used for this invention, it is possible to use independence, such as phenol resin, a cresol resin, an epoxy resin, an unsaturated polyester resin, polyimide resin, a polybutadiene resin, polyamide resin, a polyphenylene-oxide resin, and a fluororesin, a conversion object, mixture, etc., and it is suitably chosen according to a use. In this invention, the mixed ratio of the mixed spun yarn of the above-mentioned glass fiber thread and the above-mentioned organic fiber thread is suitably determined according to the resin chosen again. That is, it is determined that total of the coefficient of thermal expansion preferably divided proportionally and calculated by each volume ratio of glass fiber thread, organic fiber thread, and a resin will become zero. The laminate by this invention is manufactured according to a conventional method by the manufacturing facility of the usual glass fiber reinforcement laminate.

[0010] Although an example is shown and this invention is explained concretely hereafter, this invention is not limited to an example.

50mm chopped strand of 10 micron E glass of diameters of example fiber and theque NORA (tradename of Para system polyaramide fiber by Teijin, Ltd.) 51mm chopped fiber were opened with the opener, it measured so that it might be set to 1:1 at the rate of a volume ratio, and it considered as mixed cotton with the mixed machine. Carding of this mixed cotton was carried out with the roller card machine, the mixed sliver was created, spinning twisting was carried out with the conventional ring spinning machine, and the compound spun yarn of 71Tex (g/1000m) was obtained. Subsequently, weaving of this compound spun yarn was carried out to the textile fabrics with which ***** consists of a plain weave by density consisting of 32 diameters / 25mm, and 30 ** / 25mm, the prepreg which the epoxy resin varnish was infiltrated, and was dried and obtained was used, and the laminate of 2mm ** of 45 % of the weight of resin contents was obtained. The measurement result of the coefficient of thermal expansion of this laminate is shown in Table 1.

The prepreg which the epoxy resin varnish was infiltrated into the example plain-weave glass fiber textile fabrics of comparison (density is 44x32 [1/inch], and a weight is the style 7628 of 219 g/m2 and a product made from Asahi SHUEBERU at warp, and woof electrocardiogram75-1/0), and was dried and obtained to them was used, and the laminate of 2mm ** of 45 % of the weight of resin contents was obtained. The measurement result of the coefficient of thermal expansion of this laminate is shown in Table 1.

[0011]

[Table 1]

	熱膨張係数 (mm/mm・℃)	
	XY方向 (平面方向)	Z方向 (厚み方向)
実施例	6.5×10^{-6}	15×10^{-6}
比較例	15×10^{-6}	47×10^{-6}

[0012]

[Effect of the Invention] Since the mixed spun yarn of two sorts of specific fiber thread is used for the laminate of this invention, it has the reinforcement effect which was superior to having a low coefficient of thermal expansion when it considers as a laminate, and using spun yarn also in the thickness direction. Consequently, it is useful to the defective improvement by the difference in the coefficient of thermal expansion at the time of chip loading of the printed circuit board which used the laminate of this invention.

[Translation done.]